# STUDIES ON THE MAGNETIC BEHAVIOURS OF POTASSIUM TRIS-OXALATO-CHROMATE TRIHYDRATE IN THE RANGE OF 300° TO 90°K

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**ABSTRACT.** Following X-ray data on tris-oxalato-complexes, the magnetic measurements on potassium tris-oxalatochromate trihydrate has been carried out with the help of very sensitive anisotropy and susceptibility balances. A phase-transition is observed in the complex under investigation at about 153°K. From magnetic measurements a small anisotropy in the g-value has been calculated and a small D value (the zero field splitting) of $-0.143$ cm$^{-1}$, of the same order as in chrome alum, is observed as against the e.p.r. value of $-0.484$ cm$^{-1}$. The parametral fitting of the theory with the experimental results over the range 300°K-90°K can be obtained, only if a thermal dependence of the ligand field is postulated.

## INTRODUCTION

Magnetic measurements of the isotropic salts of chromium have been made by a number of workers, e.g. Gorter and de Haas (1930), Bagguley and Griffith (1950), Dutta Roy (1956), Mitra and Dutta Roy (1964). But little has been reported so far regarding the paramagnetic behaviour of the anisotropic salts of chromium, which alone can afford a direct knowledge of the fine structure of the ligand field levels. Ammonium tris-oxalatochromate trihydrate was first investigated by Krishnan *et al* (1939), who measured the magnetic anisotropy and susceptibility of the crystal at room and liquid oxygen temperatures. The temperature variation of magnetic anisotropy and suceptibility of ammonium and potassium tris-oxalatochromate trihydrates and vanadates were studied by Dutta Roy (1956) down to liquid oxygen temperature. Eventually, it was observed that the existing crystallographic data were in serious error (Niekerk and Schoening, 1952), so that that identification of the crystallographic axes was not correct and fresh magnetic measurements became necessary. An extensive series of accurate measurements of the magnetic anisotropy and susceptibility of a number of tris-oxalates on the basis of new crystallographic data, between the range 300°K and 90°K, were therefore undertaken in order to throw more light upon the anisotropic ligand field in these compounds. In the present paper is reported the magnetic study of one of these typical trisoxalato-complexes, viz. the potassium salt.

## PREPARATION OF THE COMPLEX AND ITS CRYSTALLOGRAPHY

The tris-oxalato-complexes have the general chemical formula $A_3M(C_2O_4)_3 \cdot 3H_2O$, where M is a trivalent metallic ion, such as $Al^{+3}$, $Cr^{+3}$, $V^{+3}$ etc. and A is a monovalent cation such as $K^+$, $NH^+_4$, $Rb^+$ etc.

Tris-oxalatochromates are prepared by first dissolving 2.3gm of potassium oxalate monohydrate and 5.5 gm of oxalic acid dihydrate in 80 ml of water. To this is added 1.9 gm of powdered potassium dichromate gradually and vigorously stirred (Booth, 1939). When the reaction is completed, the solution is evaporated nearly to dryness and allowed to crystallize at room temperature. The substance is purified by repeated crystallization and finally very good large single crystals are obtained by allowing a nearly saturated solution to evaporate slowly in a flat crystallizing basin in a dust proof and vibration free chamber. Potassium tris-oxalatochromate forms dark green almost opaque needle shaped crystals with a brilliant blue iridescence and a number of triangular faces at the ends. The crystals after being collected from the crystallizing basin are well dried and examined under a polarizing microscope for twining or other defects.

To prepare the diamagnetic isomorph potassium tris-oxalato aluminate, 1 gm of shavings of commercial aluminium is taken into a 200 ml beaker and the metal is covered with 10 ml of warm water. To this is added 30 ml of a solution of potassium hydroxide (containing 20 gm per 100ml) in portions, as vigorous effervescence subsides. Finally the solution is heated to boiling to dissolve aluminium completely. The solution is then filtered, from a residue, through a small plug of glass wool placed into the base of a funnel. Then 10 ml of water is added to the filtrate and heated to the boiling temperature. 14 gm of oxalic acid (dihydrate) is next added in portions to the hot solution, until the precipitate of hydrated alumina formed at first is just redissolved on continued boiling; excess of acid is avoided.

The neutralised solution is filtered by suction through paper from the final traces of residue and after cooling the filtrate to room temperature, 50 ml of ethanol is added to it. On continued cooling the complex oxalate separates as small colourless prisms which is then recrystallised.

The tris-oxalato-chromates were generally believed to belong to the monoclinic space group $C_{2h}^5$ (Groth 1910, Astbury 1926) the potassium salt having unit cell dimension $a:b:c = 1.0060:1:0.3989$, $\beta = 94°$, and to constitute an isomorphous series. They were found to have four molecules in the unit cell, two pairs being enantiomorphous, one pair differing from the other by a rotation of 180° about the $b$-axis. According to more recent X-ray data of Niekerk and Schoening (1952) the ammonium and potassium tris-oxalato-chromates are not only not isomorphous but the ammonium salt belongs to the triclinic space group

$P\bar{1}$, with two formula units in the unit cell, while the potassium salt belongs to the monoclinic space group $P_{2/c}$ with four formula units in the cell of dimension $a = 7.71$, $b = 19.74$, $c = 10.40$Å and $\beta = 108°$. Following the X-ray results it is found that the earlier measured unit cell size was twice the recent value (figure 1), $b$-axis remaining the same the old $c$-axis of the crystal now coincides with the new $a$-axis.

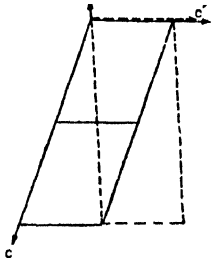


Figure 1. $a$ and $c$ indicate the new crystallographic axes and $a'$ and $c'$ the old axes.

## MEASUREMENTS OF MAGNETIC ANISOTROPY AND SUSCEPTIBILITY

In the case of high crystalline anisotropy, the well known 'Critical couple method' of Krishnan *et al* (1933) is used, where the magnetic couple is balanced against the torsional couple of the quartz suspension fibre, until a critical unstable state of the crystal under the two opposing couples is obtained and the crystal suddenly swings round to a position of more stable equilibrium. But in the present measurement the magnetic anisotropy is very small and hence the angle of twist of the quartz fibre required for balancing the magnetic couple is also correspondingly small. Thus it becomes difficult to estimate the exact magnitude of the correction term involved in the angular twist of the fibre. Hence adoption of a modified 'Null deflection method' developed in this laboratory (Datta 1954), is more suited for the present measurements. According to this method the crystal is first placed in a homogeneous horizontal magnetic field attached to the lower end of a thin long glass rod and a fine quartz fibre the upper end of which is attached to a vernier torsion head. The torsion head is rotated until the direction of maximum susceptibility in the horizontal plane is along the direction of the field. This is the setting direction and the torque on the crystal due to the field as well as the twist on the fibre is then zero. The crystal is now rotated through 45° in the absence of the field, which corresponds to maximum couple position of the crystal due to the field. The position of the crystal is then accurately determined by means of a light spot reflected by a mirror upon a balanced pair of photo cells connected across a galvanometer. With the field switched on the maximum susceptibility direction of the crystal tends to set along the field direction. The

balance in the photo-cells is disturbed as the light spot moves off the balance position causing a large deflection in the galvanometer. The original balance position is again obtained by rotating the torsion head in the opposite direction until the galvanometer deflection is brought back to zero. The anisotropy in the horizontal plane ($\Delta\chi$) is calculated from the relation

$$\Delta\chi = \frac{2Mc}{mH^2}\,\alpha_m \qquad \ldots\ (1)$$

where $\alpha_m$ is the angle of twist in the fibre required to balance the maximum couple due to the field in the 45° position, $M$ the gram molecular weight of the crystal of mass $m$, $c$ is the torsional constant of the fibre, and $H$ the value of the applied magnetic field. $H$ and $c$ are eliminated by calibrating the fibre in the same field with a crystal of $NiSO_4.6H_2O$ whose anisotropy is accurately known from earlier experiments (Datta 1956).

The anisotropy measurement has been made for two different suspensions of the crystal, with the $b$-axis, i.e. $\chi_3$—axis, vertical and again with the $a$-axis vertical. In the first position in addition to finding $\chi_1-\chi_2$ (in the (010) plane), unique determination of the value of $\theta$ the angle of orientation of $\chi_2$with respect to the $a$-axis of the crystal, is also made. With the lowering of temperature the anisotropy in the (010) plane has been found to increase and at liquid oxygen temperature the anisotropy becomes almost ten times the room temperature value. While $\theta$, which was initially 63°, is found to change by about 8° over the entire temperature range (see table 1).

A peculiar phenomenon is observed when the measurement is made with the $a$-axis of the crystal vertical to the magnetic field (see table 1). The $b$-axis, i.e. the unique $\chi_3$-axis which sets normal to the field, begins to change its setting position at about 220°K. Upto 160°K the change observed is very slow but at about 153°K a sharp change of about 75° occurs, and then the change is again found to be gradual with further fall of temperature. This large change in the angle of orientation of the $b$-axis in the field in a monoclinic crystal is quite unusual and unexpected. Another peculiarity in this mode of suspension is the gradual decrease of anisotropy in the horizontal plane with the lowering of temperature. The anisotropy is found to actually vanish at about 153°K and then change its sign, and then go on increasing upto the liquid oxygen temperature (figure 2) The crystalline anisotropy ($\chi_1-\chi_3$) obtained from the above measurement has been increasing while the temperature is decreased, but at about 153°K it shows an inflexion and then increases again (figure 3).

For the mean susceptibility measurement the powdered sample is filled tightly in a cylindrical glass container and then suspended in between the pole gap of an electromagnet, from one end of the beam of a modified balance (Mitra and Dutta Roy, 1964). The pull on this sample is then balanced by means

of a small current bearing coil fixed at the other end of the beam and placed in the pole gap of a parmanent magnet. The balancing is observed by means

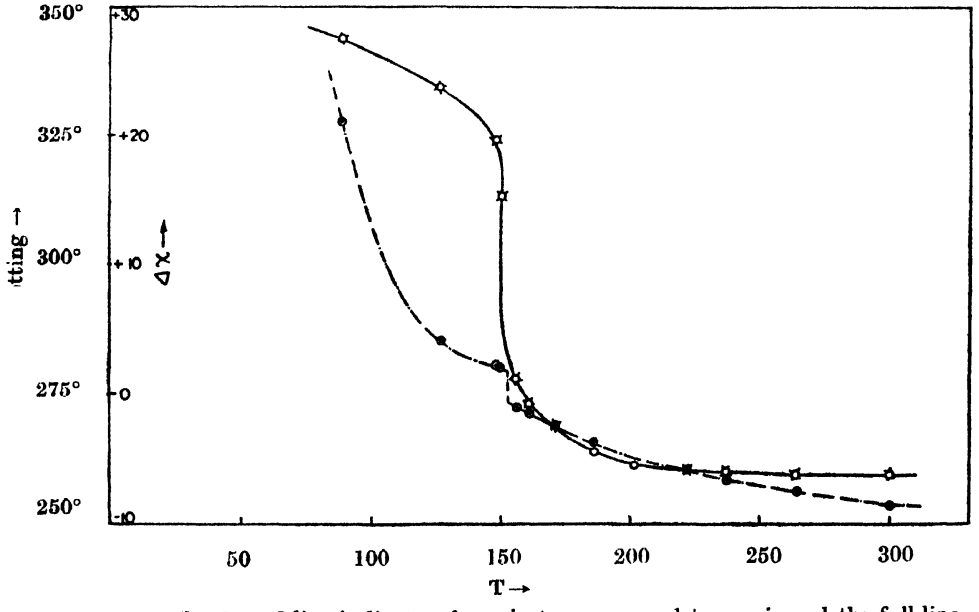


Figure 2. The dotted line indicates the anisotropy normal to *a*-axis and the full line shows the change of setting direction with *a*-axis vertical.

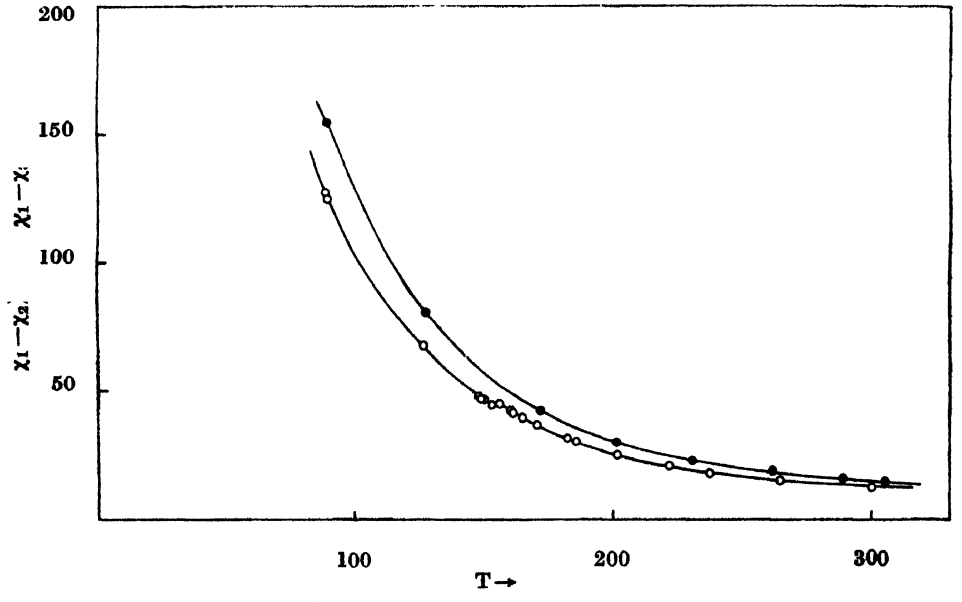


Figure 3. The lower curve shows $\chi_1-\chi_3$ and the upper $\chi_1-\chi_2$.

of a photocell arrangement. From the balancing current the mean susceptibility can be easily obtained. Anomalous magnetic behaviour is observed also

in the mean susceptibility of the tris-oxalato-complex. The susceptibility is found to increase with the lowering of temperature, but at about 153°K it becomes, practically independent of temperature for a short range of about 5°, and then the value again increases with further lowering of temperature. This peculiar behaviour is shown to an advantage in the mean moment square *versus* temperature ($p_f^2$ *vs* $T$) curve. There is a hump at about 220°K and a sharp maximum near 153°K, then it comes down almost to the room temperature value and slightly increases again as the liquid oxygen temperature is reached (fig. 4)

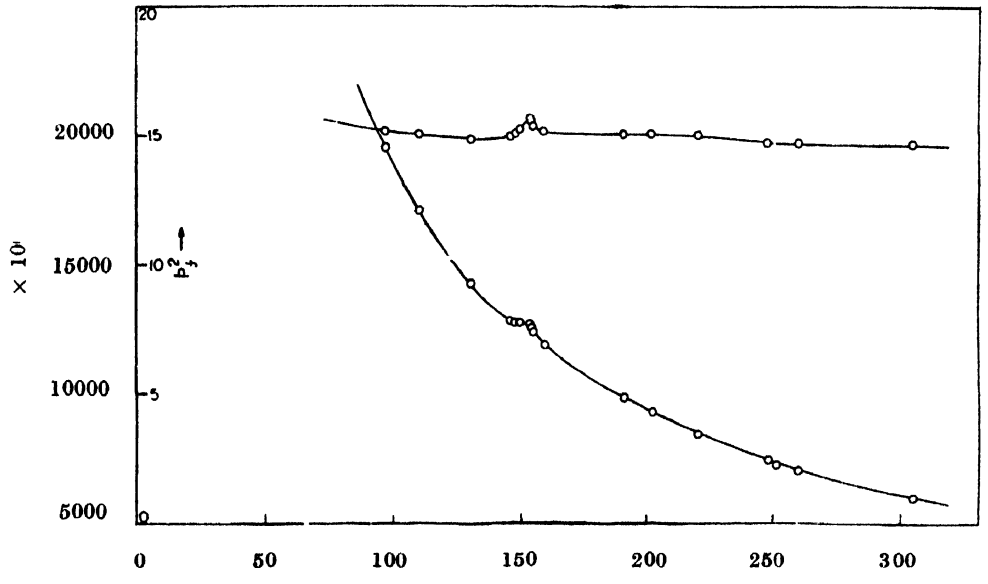


Figure 4. The mean susceptibility and the mean moment square is shown in the lower and upper curve respectively.

## CORRECTIONS FOR SHAPE AND DIAMAGNETIC ANISOTROPIES

When a crystal is placed in a nearly homogeneous magnetic field there are, in general, three different couples acting on it, viz. those due to (a) paramagnetic anisotropy (b) shape anisotropy and (c) diamagnetic anisotropy. For paramagnetic crystals of high anisotropy the last two effects constitute correction terms for the first and are negligibly small. But for the present case of low magnetic anisotropy these cannot be neglected, and an accurate estimation of the said correction is essential for accurate determination of the paramagnetic anisotropy of the crystal.

The significant part of the anisotropy of shape proportional to $\chi$ arises due to residual inhomogeneity of the magnetic field and is eliminated by cutting the crystal to a square (or round) cross section about the axis of suspension.

For the diamagnetic anisotropy correction, crystals of double tris-oxalates of $Al^{+3}$ are prepared and the diamagnetic anisotropies along different horizontal planes are accurately determined, eliminating as before the anisotropy of shape. If $(\chi_1-\chi_2)_f$ be the observed anisotropy when $b$-axis is vertical with respect to the magnetic field, $(\chi_1-\chi_2)_d$ being the diamagnetic part, and $(\chi_1-\chi_2)_s$ the paramagnetic part, then following Krishnan *et al* (1936) we have

$$(\chi_1-\chi_2)_s = (P^2+Q^2)^{\frac{1}{2}} \quad \ldots \quad (2)$$

and

$$(\chi_1-\chi_3)_s = \tfrac{1}{2}[(\chi_1-\chi_2)_s-(\chi_1-\chi_2)_f+(\chi_1-\chi_2)_d]+[(\chi_1-\chi_3)_f-(\chi_1-\chi_3)_d] \quad \ldots \quad (3)$$

where

$$P = (\chi_1-\chi_2)_d \sin 2\delta \text{ and } Q = (\chi_1-\chi_2)_f-(\chi_1-\chi_2)_d \cos 2\delta$$

$$\tan 2\sigma = P/Q$$

$\delta$ being the angle between the *observed* paramagnetic and diamagnetic $\chi_1$ axes and $\sigma$ that between *observed* and *actual* paramagnetic $\chi_1$ axes. In the table 1 the values of the anisotropies have been corrected for diamagnetism using the above formulae.

Table 1. Values of experimental crystalline anisotropies and setting angles.

| Temp. | b-axis vertical | | a-axis vertical | | |
|---|---|---|---|---|---|
| | | Setting angle | | Setting angle | |
| | $(\chi_1-\chi_2)\times 10^6$ | $\theta = \hat{a}\chi_2$ | $\Delta\chi \times 10^6$ | b axis normal to field | $(\chi_1-\chi_2)\times 10^6$ |
| 300 | 14.60 | 75.0 | 8.55 | 90.0 | 13.08 |
| 280 | 16.20 | 75.4 | 8.00 | 90.0 | 13.80 |
| 260 | 18.30 | 75.9 | 7.45 | 89.8 | 15.20 |
| 240 | 21.00 | 76.8 | 6.83 | 89.5 | 17.40 |
| 220 | 25.00 | 77.9 | 6.00 | 89.0 | 20.60 |
| 200 | 30.05 | 79.3 | 4.80 | 87.8 | 25.30 |
| 180 | 37.60 | 80.5 | 3.28 | 83.8 | 31.85 |
| 160 | 48.80 | 81.5 | 1.42 | 81.3 | 41.85 |
| 140 | 64.90 | 82.4 | − 2.43 | 24.3 | 54.10 |
| 120 | 89.30 | 83.2 | − 5.25 | 12.0 | 73.60 |
| 100 | 127.00 | 83.8 | −12.05 | 6.8 | 101.70 |
| 90 | 152.20 | 84.2 | −20.00 | 5.7 | 122.50 |

## THE THEORY OF THE LIGAND FIELD IN $Cr^{+3}$ TRISOXALATES

It is known that the $Cr^{+3}$ ion in the tris-oxalate is surrounded by an octahedron of oxygen atoms of the oxalate groups. The octahedron is slightly distorted along one of the trigonal axis and produces a predominantly cubic field about the central paramagnetic ion with a small superimposed trigonal component. Under the influence of such a field the free ion ground state $3d^3$. $^4F_{3/2}$ of the original $Cr^{+3}$ ion now splits up into an orbital singlet and two orbital triplets above it. From the e.p.r. experiment of Singer (1955) a small separation of the basic orbital singlet into two doubly degenerate Kramers spin levels (since $Cr^{+3}$ ion has three 3d electrons) is indicated. Each of the upper orbital triplets under the influence of this uniaxial field breaks up into an orbital singlet and a doublet. Of the four-fold spin degeneracy of each of the orbital levels, as already indicated, only the two-fold degeneracy is removed by the asymmetric field and the spin orbit coupling $\zeta$; the remaining two fold, being of the Kramers type, remains unaffected by the crystalline field. The effect of magnetic exchange or other types of interactions upon the spin splittings and hence on the susceptibility should be very small in case of such a fairly diluted crystal .

Dutta Roy (1956) tried to explain his experimental results on the mean susceptibilities of $Cr^{+3}$ alums with the help of an equation derived from Van Vleck's theory on the assumption of a trigonally distorted octahedral field. But he did not consider the effect of covalency upon the magnetic behaviours. We have in the present used the Spin Hamiltonian approximation, taking into consideration the overlap between 3d charge cloud of $Cr^{+3}$ and 4s, 4p clouds of ligand oxygens and arrived at the following three coefficient formulae for the anisotropy and the mean susceptibility of $Cr^{+3}$ tris-oxalato complex which we proceed next to compare with our experimental data.

$$K_{\parallel} = N\beta^2 \left( -2\alpha_{\parallel}\epsilon_{\parallel}^2 + \frac{5g_{\parallel}^2}{4kT} - \frac{g_{\parallel}^2 D}{k^2T^2} \right) \quad \ldots \quad (4a)$$

$$K_{\perp} = N\beta^2 \left( -2\alpha_{\perp}\epsilon_{\perp}^2 + \frac{5g_{\perp}^2}{4kT} + \frac{g_{\perp}^2 D}{k^2T^2} \right) \quad \ldots \quad (4b)$$

$$K_{\parallel} - K_{\perp} = N\beta^2 \left[ -2(\alpha_{\parallel}\epsilon_{\parallel}^2 - \alpha_{\perp}\epsilon_{\perp}^2) + \frac{5}{4kT}(g_{\parallel}^2 - g_{\perp}^2) - \frac{D}{k^2T^2}(g_{\parallel}^2 + g_{\perp}^2) \right] \ldots \quad (4c)$$

and $$\bar{K} = 1/3(K_{\parallel} + 2K_{\perp}) \quad \ldots \quad (4d)$$

where $$g_{\parallel} = 2(1+\zeta_{\parallel}\alpha_{\parallel}\epsilon_{\parallel})$$

$$g_{\perp} = 2(1+\zeta_{\perp}\alpha_{\perp}\epsilon_{\perp})$$

and $$D = (\alpha_{\perp}\zeta_{\perp}^2 - \alpha_{\parallel}\zeta_{\parallel}^2)$$

Here $\alpha_{||}$ and $\alpha_{\perp}$ are the coefficients of anisotropic ligand field used by Schlapp and Penney (1932), $\epsilon_{||}$ and $\epsilon_{\perp}$ are the orbital reduction factors, $\zeta_{||}$ and $\zeta_{\perp}$ being anisotropic spin orbit coupling coefficients in the crystal including reduction factors arising from the overlapping of ligand charge clouds with the 3*d* charge cloud of the central ion. The suffixes || and $\perp$ all through mean the values of respective quantities along and perpendicular to the trigonal field axis.

Table 2. Ionic anisotropy, mean susceptibility, effective mean moment square and inter ionic angle.

$g_{||} = 1.9607$ $\quad \zeta_{||} = +85.0\ \text{cm}^{-1}$ $\quad \alpha_{||} = -2.688\times10^{-4}\ \text{cm}$ $\quad \epsilon_{||} = .86$

$g_{\perp} = 1.9582$ $\quad \zeta_{\perp} = +81.8\ \text{cm}^{-1}$ $\quad \alpha_{\perp} = -3.116\times10^{-4}\ \text{cm}$ $\quad \epsilon_{\perp} = .82$

$g = 1.959,$ $\quad \lambda = 91\ \text{cm}^{-1}$ (free ion) $\quad E_1 - E_2 = 17500\ \text{cm}^{-1},$

$E_1 - E_3 = 23900\ \text{cm}^{-1}$ (spectroscopic value) $\quad D = -0.143\ \text{cm}^{-1}$

| | Calculated Experimental | | Calculated Experimental | | | |
|---|---|---|---|---|---|---|
| Temp. | $(K_{||}-K_{\perp})\times10^6$ | $(K_{||}-K_{\perp})\times10^6$ | $\bar{K}\times10^6$ | $K\times10^6$ | $p_f^2$ | $2\phi$ |
| 300 | 16.30 | 16.40 | 6103 | 6100 | 14.69 | 37°07′ |
| 280 | 18.38 | 18.80 | 6531 | 6520 | 14.70 | 42°49′ |
| 260 | 20.86 | 21.40 | 7025 | 7020 | 14.71 | 44°45′ |
| 240 | 23.82 | 24.90 | 7601 | 7700 | 14.80 | 45°40′ |
| 220 | 27.53 | 29.30 | 8283 | 8530 | 14.98 | 45°20′ |
| 200 | 32.57 | 34.50 | 9162 | 9420 | 15.04 | 44°50′ |
| 180 | 38.65 | 43.30 | 10170 | 10410 | 15.06 | 42°45′ |
| 160 | 46.78 | 55.60 | 11430 | 11800 | 15.15 | 40°56′ |
| 140 | 58.09 | 75.60 | 13040 | 13300 | 14.89 | 44°18′ |
| 120 | 74.65 | 105.00 | 15200 | 15470 | 14.81 | 45°30′ |
| 100 | 100.71 | 152.30 | 18210 | 18950 | 15.14 | 48°66′ |
| 90 | 119.91 | 182.20 | 20220 | 21140 | 15.28 | 48°16′ |

## DISCUSSION OF THE RESULTS

Each of the two inequivalent chromium tris-oxalato-complex has one unique 3-fold axis of rotational symmetry, so that the crystalline field acting on each $Cr^{+3}$ ion may be taken to have a trigonal symmetry. Paramagnetic resonance experiment (Singer 1955) is not able to detect any anisotropy in the *g* factor which comes out as 1.983. But the sign of $D(=\alpha_{\perp}\zeta_{\perp}^{\ 2}-\alpha_{||}\zeta_{||}^{2})$ the zero field splitting, is found to be negative. $\alpha_{||}$ and $\alpha_{\perp}$ are negative and numerically

$\alpha_\perp > \alpha_\parallel$ as indicated by the X-ray observation (Niekerk and Schoening 1952) that the ligand octahedron is slightly elongated along a trigonal axis, and also because the alternative assumption $\alpha_\parallel > \alpha_\perp$ numerically, leads to unreasonable values of the field parameters in equations. (4a—c). It follows that $K_\parallel > K_\perp$ and we then have the relations

$$K_\parallel - K_\perp = 2(\chi_1 - \chi_2) - (\chi_1 - \chi_3) \tag{5}$$

and

$$\cos 2\phi = \frac{\chi_1 - \chi_3}{K_\parallel - K_\perp}$$

where $2\phi$ is the angle of orientation between the two trigonal axes of the inequivalent ions. The values of $K_\parallel - K_\perp$ and $2\phi$ calculated for $Cr^{+3}$ ion at different temperatures at intervals of 20° obtained from the smoothed out graph for $(\chi_1 - \chi_2)$ and $(\chi_1 - \chi_3)$ against temperature are given in table 2. The angle $2\phi$ is found to increase initially with the lowering of temperature and on reaching 220°K it decreases with further decrease of temperature. At 140°K it is again found to increase continuously down to the lowest temperature of our experiment. These changes in the value of $2\phi$ are evidently caused by progressive rearrangement of the atoms associated with the final phase transition of the crystal. These are shown in table 2. The experimental values of ($\bar{K}$ and $K_\parallel - K_\perp$) are fitted at 300°K, with the theoretical formula with a given set of the parameters $g_\parallel$ $g_\perp$ ; $\zeta_\parallel$, $\zeta_\perp$ and $D$ near room temperature, since additional spectroscopic absorption data Jφrgensen, 1962 are available for some of the above parameters at that temperature serving as a check. The values of $\bar{K}$ and $(K_\parallel - K_\perp)$, both experimental and calculated from the theory, are shown in table 2. It is observed that with the same set of parameters the experimental values at other temperatures differ considerably from the calculated ones. This is obviously related to the phase transition occuring at 153°K. The deviation actually becomes more and more prominent as the transition temperature is approached and crossed over.

A modification of monoclinic symmetry is apparent from the measurement of the anisotropy of the crystal with $a$-axis vertical to the magnetic field. Now the $b$-axis lies in the horizontal plane. Since the $b$-axis coincides with the $\chi_3$-axis above the transition, it should set either parallel or perpendicular to the magnetic field. In actual experiment, however, the $\chi_3$-axis rotates, at first slowly and then very rapidly, showing that the $b$-axis no longer remains a symmetry axis (figure 2). The observation that the anisotropy in the plane normal to $a$-axis gradually falls down to zero and changes sign after the transition temperature is passed, shows that $(\chi_1 - \chi_2)\sin^2\theta$ which is at the beginning less than $\chi_1 - \chi_3$ tends to become equal to it at 153°K and then becomes greater. It is of course to be remembered that this is a continuous type of reversible transition and the formula used for the anisotropy calculation for a monoclinic crystal is not strictly valid at lower tempera-

tures when transition has started, so that our above statements are only approximate and qualitative ones. Our main aim here is to bring out the broad fact that the thermal expansions and rearrangements of the charges in the lattice are quite often of the greatest importance in changing the nature and magnitude of the ligand fields in the crystals and this is shown in a startling manner in this salt.

The X-ray data on this trisoxalato-complex taken in our laboratory confirms that there is a transition from a higher to a lower symmetry at low temperature. The detailed X-ray investigation on this transition is in progress. When these are available a better fitting of the experimental data with a theory which takes into consideration the changes in the ligand field parameters with temperature will be possible.

The small anisotropy in the $g$-value observed from magnetic anisotropy data is too small to be measured by the e.p.r. technique (Singer 1955). The mean value of $g = 1.983$ observed by Singer at room temperature is quite inconsistent with the mean calculated from our principal values, viz. $g_{\parallel} = 1.9607$ and $g_{\perp} = 1.9582$ and also with the spectroscopic absorption levels shown over table 2, with which our $g$ values check well. These latter are not so different from the corresponding data in chrome alum. Moreover, Singer's mean value is so close to the spin only value of 2.0023 that it leads to an unreasonably low value of the spin-orbit reduction factor. The zero field splitting $D = -0.484$ cm$^{-1}$ obtained by Singer also differs considerably from $D = \cdot 0.143$ cm$^{-1}$ obtained from magnetic anisotropy measurements. The latter value, however, agrees well with the $D$ value for the chromium alums showing that the anisotropic ligand field in the two cases are not very different. Thus we see that for low anisotropic complexes the direct magnetic measurements are much more reliable and instructive for the purpose of elucidating the asymmetric ligand fields in $Cr^{3+}$ complexes. Values of the spin orbit coupling coefficients $\zeta_{\parallel}$ and $\zeta_{\perp}$ are found to be affected by the anisotropic overlap of the $3d$ charge cloud with those of the ligands, (table 2). More detailed fittings and theoretical discussions with reference to the refined theory developed by some of our co-workers will be undertaken in the near future.

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